Catalytic Activities of a Polyoxime-cobalt Complex for the Addition Reaction of an Alcohol to Acrylaldehyde and for the Polymerization of Styrene

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(Received March 14, 1974)

A new polymeric cobalt-chelate complex was prepared from cobalt acetate and a polyoxime consisting mainly of 1,2-bis(hydroxyimino)trimethylene units. The polymeric complex in the solid state at 77—300 K, both in air and under a vacuum, gives an ESR signal with a *g*-value of about 2 and can initiate the polymerization of styrene and catalyze the "Michael"-type addition reaction of an alcohol to acrylaldehyde, yielding exclusively β-alkoxypropionaldehyde, after being treated with phenylthiol and sodium borohydride. The catalytic activities depend greatly on the cobalt content and are much greater than those of its monomeric analogue in composition, bis(dimethylglyoximato)cobalt. The absorption spectrum of the polymeric complex treated with the reagents is similar to that of monomeric or polymeric analogues containing monovalent cobalt atoms.

The metal-chelate complexes of a new polyoxime have been investigated in terms of physical and chemical properties in comparison with those of the monomeric analogues corresponding in composition, the metal-chelate complexes of dimethylglyoxime. The polyoxime was derived from an alternating copolymer of ethylene and carbon monixide ($\left[-(CH_2CH_2)_{1.2}-\underset{\underset{O}{\|}}{C}-\right]_x$, $(C_{17}H_{24}O_5)_x$, $(308.4)_x$, molecular weight 4000): it is considered to consist mainly of 1 2-bis(hydroxyimino)trimethylene units ($\left[-(CH_2)_{1.6}-(\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C})_{0.8}-(\underset{\underset{O}{\|}}{C})_{0.2}-\right]_x$, $(C_{17}H_{24}N_8O_9)_x$, $(484.3)_x$). A reversible uptake of molecular oxygen by a polyoxime-cobalt complex(POX-Co) and catalytic activities of a polyoxime–copper complex have been reported.[1–3)]

$$CO + C_2H_4 \longrightarrow -CH_2CH_2-\underset{\underset{O}{\|}}{C}- \longrightarrow$$

$$-CH_2-\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}- \xrightarrow{Co(CH_3CO_2)_2\cdot 4H_2O} \text{POX-Co}$$

Here we will describe the catalytic activities of POX-Co in the polymerization of styrene and in the "Michael"-type addition reaction of an alcohol to acrylaldehyde, yielding exclusively β-alkoxypropionaldehyde. A di- or trivalent cobalt complex of dimethylglyoxime (cobaloxime (II) or (III)) can be converted into a monovalent cobaloxime(I) by treatment with reductants.[4)] On the other hand, POX-Co does not show any change upon treatment with reductants alone. However, a combination of sodium borohydride and a polymeric complex prepared by the treatment of POX-Co with phenylthiol(POX-Co-S) or the resulting complex(POX-Co-R) shows catalytic activities.

Experimental

Materials. By adding 4.5, 2.5, 1.5, 1.2, or 0.8 g of bis(acetate) tetraaquocobalt ($Co(CH_3CO_2)_2 4H_2O$) into a solution of 3.0 g of the polyoxime in a mixture of dioxane and methanol (1:1 by volume, 5×10^{-3} g/ml) under nitrogen, a complex with a cobalt content of 19.12 (POX-Co-1), 14.84 (POX-Co-2), 10.38 (POX-Co-3), 7.83 (POX-Co-4), or 5.71% (w/w) (POX-Co-5) was prepared; these complexes correspond to the complexes with the composition ratios of Co*/OX=1/4, 1/6, 1/8, 1/12, and 1/16 (where Co* and OX are the numbers of cobalt atoms and oxime groups in the complex). The catalysts employed were derived from POX-Co-1—5. As an example, the preparation of the catalyst derived from POX-Co-1 will be described. In a 50 ml flask we placed 1.0 g of POX-Co-1, 1.0 g of phenylthiol (excess) and 20 ml of methanol. The mixture was then stirred at room temperature for 24 hr under nitrogen. This yielded a red-purple powder, which was then separated by filtration, washed with methanol, and dried at 80 °C for 8 hr *in vacuo* (yield: 1.5 g, POX-Co-S-1). POX-Co-1 has a composition corresponding to a cobalt/phenylthio group of *ca.* 1/1. The IR spectrum of POX-Co-S-1 showed characteristic bands of the phenyl group (3040, 1485, 735, and 685 cm^{-1}, KBr disc). In a 50 ml flask we placed 1.6 g of POX-Co-S-1 with a cobalt content of 14.59%, 75 mg of $NaBH_4$ (a slight excess), and 20 ml of isopropyl alcohol. The mixture was stirred for 4 hr at 70 °C under nitrogen. After 0.5 hr it changed into a green solution (probably monovalent cobalts are present); the brown precipitate which was deposited was then washed with 1% of acetic acid and water and dried at 80 °C for 8 hr over P_2O_5 *in vacuo* (yield: 1.0 g POX-Co-R-1). The results of the elemental analysis and the IR spectrum of POX-Co-R-1 were almost the same as those of POX-Co-1. When the mixture was stirred in air, phenyldithiobenzene was formed catalytically, and the resulting red-purple powdery complex, with IR spectrum and elemental analysis almost the same as those of POX-Co-S-1, did not show any change upon treatment with $NaBH_4$. The other catalysts, with lower cobalt contents, POX-Co-S-2—5 and POX-Co-R-2—5, were derived from POX-Co-2—5 similarly. In the preparation of POX-Co-S-2—5, 280 (POX-Co-S-2), 210 (POX-Co-S-3), 140 (POX-Co-S-4) or 105 mg (POX-Co-S-5) of phenylthiol per 1.0 g of POX-Co-2—5 was employed; in that of POX-Co-R-2—5, a slight excess of $NaBH_4$ was used. These catalysts are insoluble powders. The elemental analyses of these compounds are summarized below. Found Copolymer: C, 65.80; H, 7.58%. Calcd for $\left[-(CH_2CH_2)_{1.2}-\underset{\underset{O}{\|}}{C}-\right]_x$, $(C_{17}H_{24}O_5)_x$, $(308.4)_x$: C, 66.23; H, 7.79%. Found Polyoxime: C, 42.51; H, 4.98; N, 22.54%. Calcd for $\left[-(CH_2)_{1.6}-(\underset{\underset{HON}{\|}}{C})_{1.6}-(\underset{\underset{O}{\|}}{C})_{0.2}-\right]_x$, $(C_{17}H_{24}N_8O_9)_x$, $(484.4)_x$: C, 42.15; H, 4.96; N, 23.14%. Found POX-Co-1: C, 34.35; H, 3.87; N, 18.15; Co, 19.12%. POX-Co-R-1: C, 33.86; H, 3.91; N, 18.36, Co, 19.38%. Calcd for Co*:OX=1:4, $(C_{17}H_{20}N_8O_9Co_2)_x$, $(598.3)_x$: C, 34.13; H, 3.37; N, 18.73; Co, 19.70%. Found POX–Co-S-1: C, 42.78; H, 4.16; N, 16.85; Co, 14.59; S, 7.76%. Calcd for Co*: OX: S* = 1: 4: 1, $(C_{29}H_{30}N_8O_9S_2Co_2)_x$, $(816.5)_x$: C, 42.66; H, 3.70; N, 17.24; Co, 14.43, S, 7.85%. Found POX–Co-2: Co, 14.16%. POX–Co-R-2: Co, 14.12%. Calcd for Co*: OX = 1: 6: Co, 14.02%. Found POX–Co-S-2: Co, 11.20; S, 6.25%. Calcd for Co*: OX: S* = 1: 6: 1: Co, 11.34; S, 6.18%. Found POX–Co-3: Co, 10.38%. POX–Co-R-3: Co, 10.27%. Calcd for Co*: OX = 1: 8: Co, 10.89%. Found POX–Co-4: Co, 7.58%. POX–Co-R-4: Co, 7.42%. Calcd for Co*: OX = 1: 12: Co, 7.52%. Found POX–Co-S-4: Co, 6.51; S, 3.64%. Calcd for Co*: OX: S* = 1: 12: 1: Co, 6.48; S, 3.53%. Found POX–Co-5: Co, 5.53%. POX–Co-R-5: Co, 5.42%.Calcd for Co*: OX = 1: 16: Co, 5.45%. Found POX–Co-S-5: Co, 4.86; S, 2.73%. Calcd for Co*: OX: S* = 1: 16: 1: Co, 4.83; S, 2.63% (S*: number of sulfur atoms.).

Procedures. *Polymerization*: In a three-necked flask equipped with a condenser, a gas-inlet tube, and a dropping funnel containing redistilled styrene, we placed the catalyst, the medium and the other reactants ($NaBH_4$, aq NaOH, *etc.*). The amounts of these reactants are given in Table 1. The mixture was stirred at 70 °C under nitrogen; after 0.5 hr it changed into a green solution (probably monovalent cobalts are present). The styrene was then added. After 3.0 hr the mixture was poured into methanol, and the resulting precipitate was collected by filtration. The precipitate was put in hot toluene, and the resulting solution was filtered to remove the catalyst. The filtrate was concentrated and then poured into methanol, after which the precipitated polystyrene (molecular weight, 5200—7400) was collected by filtration.

Addition Reaction: In a 25-ml glass tube we placed 0.1 g of POX–Co-R, 1/10 mol of purified acrylaldehyde, and 1/5 mol of an alcohol. The tube was then swept free of air with nitrogen, sealed, and stirred at 60—70 °C for 2 hr in a water bath. The product was characterized using IR, NMR, and gaschromatographic techniques.

Measurement. The absorption spectrum was measured at room temperature under nitrogen using a Cary-11 Recording Spectrophotometer. The ESR spectrum was taken with a Nihon Denshi Electron Spin Resonance Spectrometer, Model JEOL-P-10 X-band, using the 100 kHz field. The molecular weights of the ethylene/carbon monoxide copolymer and the polystyrene were determined using a Perkin-Elmer Molecular Weight Apparatus.

TABLE 1. POLYMERIZATION OF STYRENE

Catalyst system	Medium[b) ROH, R=	Product PS[c) (g)/Co (gram atom)
PhS–Co–Pyr[d) + I[e)	i-C_3H_7	4.0×10^3
PhS–Co–Ryr+I+II[f)	i-C_3H_7	3.4×10^3
POX–Co-S-1+I+II	CH_3	—
-S-1+I	i-C_3H_7	14.7×10^3
-S-1+I	t-C_4H_9	19.1×10^3
-S-1+I+II	i-C_3H_7	$26.0\times10_3$
-S-2+I+II	i-C_3H_7	7.0×10^3
-S-5+I+II	i-C_3H_7	0.2×10^3
POX-Co-R-1	i-C_3H_7	1.0×10^3
-R-1+I	i-C_3H_7	24.8×10^3
-R-1+II	i-C_3H_7	10.8×10^3
-R-2+II	i-C_3H_7	3.9×10^3
-R-3+II	i-C_3H_7	0.5×10^3
-R-4+II	i-C_3H_7	0.1×10^3

a) Carried out at 70 °C for 3 hr under nitrogen. b) 20 ml of each alcohol was used. c) Polystyrene. d) Phenylthiolatopyridinatocobaloxime.[5) e) 50 mg of $NaBH_4$. f) 1.0 ml of 15%(w/w) aq. NaOH. Catalysts used : 100 mg, Styrene used: 10.0 g.

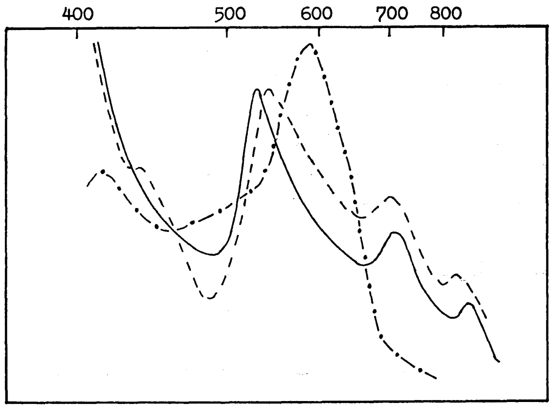


Fig. 1. Absorption spectra.
——: The green solution obtained by the reaction of POX–Co-S-1 with $NaBH_4$ (in 2-propanol).
----: Vitamine B_{12s} (in methanol)[6)
-●-: Tributylphosphinatocobaloxime(I) (in methanol)[6).

Results and Discussion

Table 1 shows that the polymeric complexes are much more effective than cobaloximes; this is obvious in the catalyst systems including a strong alkali. The addition of 1.0 ml of 15% aqueous potassium hydroxide or 300 mg of sodium isopropoxide instead of 15% aqueous sodium hydroxide had the same enhancing effect; however that of 1.0 ml of aqueous lithium hydroxide or calcium hydroxide did not. The absorption spectrum of the green solution obtained as a result of the reaction of POX–Co-S, POX–Co-R or phenylpyridinatocobaloxime(III) with sodium borohydride is similar to that of a cobaloxime(I) or vitamine B_{12s} (containing a Co(I)),[6) as is shown in Fig. 1. The formation of a cobaloxime(III) with a Co–C bond resulting from the reaction of a cobaloxime(I) with styrene has also previously been shown.[7) These facts suggest that a species containing a Co(I) plays an important role in the polymerization. It is well known that unstable monomeric binuclear Co(II) complexes including a cobaloxime(II) disproportionate into a Co(I) and a Co(III) complex in a strong alkaline solution.[8) POX–Co-R may consist partly of binuclear Co(II) units, which might contribute to make the polymeric catalyst more effective. However, a system containing a binuclear cobaloxime(II) (dimeric pyridinato- or aquocobaloxime(II)) could not polymerize styrene under the same conditions as those employed for the polymeric catalyst. POX–Co-R can be converted into POX–Co-S again by the addition of phenylthiol under nitrogen; this is supported by a comparison of their elemental analyses, IR spectra, and reactivities towards sodium borohydride.

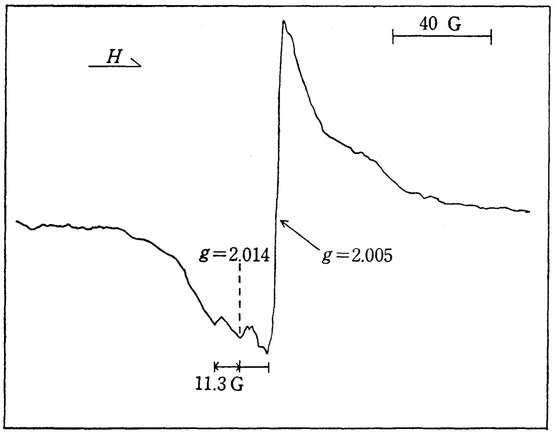
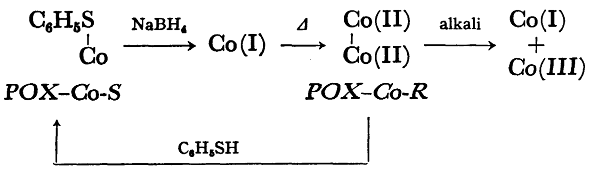


Fig. 2. ESR spectrum of the polyoxime–cobalt complex (POX-Co-R-1). Measured in the solid state (powder) at 77 K under vacuum.

Table 2. "Michael" type addition reaction of an alcohol to acrylaldehyde[a)]

Catalyst	Alcohol, ROH R=	Product, $ROCH_2CH_2CHO$ mol/gram atom of Co
POX-Co-1	CH_3	0.1×10
POX-Co-R-1	CH_3	13.1×10
-R-1	C_2H_5	2.2×10
-R-1	i-C_3H_7	0.1×10
-R-1	n- or t-C_4H_9	—
-R-2	CH_3	15.2×10
-R-3	CH_3	14.9×10
-R-4	CH_3	0.1×10
-R-5	CH_3	—

Catalyst used: 100 mg. ROH used: 1/5 mol. Acrylaldehyde used: 1/10 mol. a) Carried out at 60—70 °C for 2 hr under nitrogen.



This interconversion was also confirmed by ESR spectroscopy. POX-Co-R exhibits an ESR signal at 77—300 K both in air and under a vacuum, as is shown in Fig. 2. The signal disappears as a result of the interconversion of POX-Co-R into -Co-S. The intensity of the signal increased with an increase in the cobalt content of the complex. The signal may be due to the low spin Co(II) of some units of POX-Co-R.

In the addition reaction, contrary to the results for the polymerization, the catalytic activity of POX-Co-R is not proportional to the cobalt content, and methanol is the most reactive among the alcohols used, as is shown in Table 2. When acrylonitrile, methyl acrylate or crotonaldehyde was employed instead of acrylaldehyde, it was recovered unchanged. On the other hand, bis(dimethylglyoximato)cobalt(II),[8)] which may be the monomeric analogue of POX-Co-R-1 in composition, and cyanopyridinato- and chloropyridinatocobaloxime-(III)[9)] catalyze like ordinary base-catalysts, such as sodium hydroxide and sodium acetate, the addition reaction of an alcohol not only to acrylaldehyde but also to acrylonitrile and methyl acrylate. The different behavior of the polymeric complexes in both catalyses must be partly ascribed to the varieties in the structure and properties of their units; however, there is, so far, no satisfactory explanation of the difference.

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